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An improved density matrix functional by physically motivated repulsive corrections

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An improved density matrix functional [correction to Buijse and Baerends functional (BBC)] is proposed, in which a hierarchy of physically motivated repulsive corrections is employed to the strongly overbinding functional of Buijse and Baerends (BB). The first correction C1 restores the repulsive exchange-correlation (xc) interaction between electrons in weakly occupied natural orbitals (NOs) as it appears in the exact electron pair density ρ_2 for the limiting two-electron case. The second correction C2 reduces the xc interaction of the BB functional between electrons in strongly occupied NOs to an exchange-type interaction. The third correction C3 employs a similar reduction for the interaction of the antibonding orbital of a dissociating molecular bond. In addition, C3 applies a selective cancellation of diagonal terms in the Coulomb and xc energies (not for the frontier orbitals). With these corrections, BBC still retains a correct description of strong nondynamical correlation for the dissociating electron pair bond. BBC greatly improves the quality of the BB potential energy curves for the prototype few-electron molecules and in several cases BBC reproduces very well the benchmark *ab initio* potential curves. The average error of the self-consistent correlation energies obtained with BBC3 for prototype atomic systems and molecular systems at the equilibrium geometry is only ca. 6%. © *2005 American Institute of Physics*.
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I. INTRODUCTION

Starting from the pioneering work of Heitler and London,[1] one of the paradigmatic problems of quantum chemistry has been the correct description of electron correlation in the electron pair bond. The correct description of left-right correlation manifests itself in the occurrence of certain orbital products in the pair density (diagonal two-electron reduced density matrix) $\rho_2(1,2)$. In particular, the double excitations that are well known to provide the primary correlating configurations in the wave function, lead to orbital product terms in the pair density that are crucial for the left-right correlation. The proper dissociation wave function for H_2 at $R\to\infty$, $\Psi=c_g|\sigma_g(1)\overline{\sigma}_g(2)|+c_u|\sigma_u(1)\overline{\sigma}_u(2)|$, where $\sigma_g=1/\sqrt{2}(a+b)$ and $\sigma_u=1/\sqrt{2}(a-b)$ (a and b are the atomic orbitals), leads in the pair density $\rho_2(1,2)=2\Psi(1,2)\Psi(1,2)^*$ to diagonal terms such as $|c_g|^2\sigma_g(1)\overline{\sigma}_g(2)\sigma_g^*(1)\overline{\sigma}_g^*(2)$ and $|c_u|^2\sigma_u(1)\overline{\sigma}_u(2)\sigma_u^*(1)\overline{\sigma}_u^*(2)$. These diagonal terms do not, for a reference electron at one site, differentiate between the probabilities of finding the other electron at the same site or the other site. If, for instance, electron 1 is at a position in the neighborhood of nucleus a with spin α, i.e., $\mathbf{r}_1\in\Omega_a, s_1=\alpha$, then the conditional probability $\rho_2^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)/\rho_1^{\alpha}(\mathbf{r}_1)$ of finding electron 2 at position $2=\mathbf{r}_2,s_2$ is, when electron 2 has β spin, $1/2|a(\mathbf{r}_2)|^2+1/2|b(\mathbf{r}_2)|^2$, i.e., an even distribution over the two sites (of course there is zero probability for the second electron to be anywhere with α spin). However, the cross products $c_gc_u^*\sigma_g(1)\overline{\sigma}_g(2)\sigma_u^*(1)\overline{\sigma}_u^*(2)+$c.c. do make the left-right distinction. With the limiting values $c_g\approx -c_u\approx 1/\sqrt{2}$, the cross terms yield for the conditional density of the β spin electron the contribution $-1/2[\sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\sigma_u^*(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_2)+\text{c.c.}]/\rho_1^{\alpha}(\mathbf{r}_1)$, which correctly has a negative lobe around the reference electron at $\mathbf{r}_1$, while its positive lobe is on the remote atom: i.e., when $\mathbf{r}_1$ is in the neighborhood of atom H_A, $\mathbf{r}_1\in\Omega_a$, $s_1=\alpha$, the contribution is $-1/2|a(\mathbf{r}_2)|^2+1/2|b(\mathbf{r}_2)|^2$, and when $\mathbf{r}_1\in\Omega_b$, the contribution is $1/2|a(\mathbf{r}_2)|^2-1/2|b(\mathbf{r}_2)|^2$. So these cross product terms take care, when added to the even distribution from the diagonal terms, that the probability for an electron with spin down to be on nucleus b is 1 when the electron of up-spin is known to be on nucleus a, and vice versa. In atoms, such orbital cross products, stemming from double excitations, also take care of in-out correlation, for instance, the $1s^2\to ns^2$ excitations in He, and of angular correlation around the nucleus, e.g., the $1s^2\to np^2$ excitations in He.[2] Evidently, in any theory that directly tries to express the pair density in terms of orbitals, the occurrence of these orbital cross products in the trial two-matrix must play a key role.

For two-electron systems, it has been shown by Löwdin and Shull[3] in one of the first applications of the concept of natural orbitals (NOs) that the exact two-electron closed-shell wave function $\Psi(1,2)$ reduces to just a summation over excited closed-shell configurations, when the NOs are used as an expansion basis,

$$\Psi(1,2) = \sum_i c_i |\chi_i(1)\overline{\chi_i}(2)|. \tag{1.1}$$

Here χ_i are the NOs with their occupations n_i, which can be easily deduced to be $n_i = 2c_i^2$ (we refer to Ref. 4 for the use of reduced density matrices in the treatment of electron correlation). The exact spin-free ρ_2 corresponding to Eq. (1.1) contains, in particular, the cross products $-[\sqrt{n_1 n_a}\chi_1(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_a^*(\mathbf{r}_1)\chi_a^*(\mathbf{r}_2) + \text{c.c.}]$ between the first NO χ_1, with the largest occupation n_1, and other NOs χ_a. In the case of nondynamical correlation in dissociating H_2 we have just $\chi_1 = \sigma_g$ and $\chi_a = \chi_2 = \sigma_u$. In another limiting case, the He isoelectronic series, the terms $-[\sqrt{n_1 n_a}\chi_1(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_a^*(\mathbf{r}_1)\chi_a^*(\mathbf{r}_2) + \text{c.c.}]$, being the only explicitly negative contributions to the electron-electron interaction energy calculated with Eq. (1.1), are, apparently, also responsible for the dynamical correlation prevailing in that case. This time, however, many terms with weakly occupied NOs are relevant.

In density matrix functional theory (DMFT) one tries to obtain approximations to the pair density using the NOs and NO occupation numbers. It is very important that such approximations contain the essential physics of electron correlation, and they should therefore retain the correlating orbital products just noted. In order to arrive at a useful approximation of ρ_2, Buijse and Baerends[2,5,6] wrote for closed-shell systems the related exchange-correlation (xc) hole function $\rho_{\text{xc}}^{\text{hole}}(\mathbf{r}_2|\mathbf{r}_1)$ as the square of a hole amplitude $\varphi_{\text{xc}}^{\text{hole}}(\mathbf{r}_2;\mathbf{r}_1)$ and expanded the amplitude describing the hole around a position $\mathbf{r}_1$, in the complete set of NOs (see the following section for the corresponding expressions). This is a generalization of the case of the pure exchange hole, where the exact hole can be expanded in just the occupied Hartree–Fock orbitals.[7] With the expansion coefficients obtained with due account of the "sum rule" and the permutation symmetry for the two-matrix, Buijse and Baerends (BB) expressed the total pair density ρ_2 in the following form:

$$\rho_2^{\text{BB}}(\mathbf{r}_1,\mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \sum_{i,j} \sqrt{n_i n_j}\chi_i^*(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j^*(\mathbf{r}_2), \tag{1.2}$$

where the natural occupation numbers $\{n_i\}$ are constrained to lie between 0 and 2.

This particular functional has been obtained by Müller[8] in a completely different way. Csanyi and Arias[9] considered the formal symmetry properties of two-matrices that are written as tensor products of one-matrices and arrived at what they called the corrected Hartree (CH) functional, which is identical to Eq. (1.2), as the simplest case. The ansatz (1.2) contains orbital cross products such as $-[\sqrt{n_i n_a}\chi_i(\mathbf{r}_1)\chi_a^*(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_a^*(\mathbf{r}_2) + \text{c.c.}]$ between strongly occupied NOs χ_i, $i \leqslant N/2$, and weakly occupied NOs χ_a, $a > N/2$, which are similar, apart from different complex phases, to the orbital products highlighted above. The importance of these cross products to describe correlation has been emphasized,[2] and they need to be retained, but due to other approximations made (see the following section for discussion), the BB two-matrix (1.2) overestimates the xc effect.

Goedecker and Umrigar[10] (GU) have modified the BB xc functional by omitting certain diagonal ($i=j$) terms in both the expansion of $|\Omega_{\text{xc}}^{\text{hole}}(\mathbf{r}_2;\mathbf{r}_1)|^2$ and in the Hartree energy. This modification tends to improve the energies but has the disadvantage that the functional is no longer self-interaction free (the GU modification has been called a "self-interaction correction," but in a certain sense this is a misnomer since the modification destroys the integration of the exchange-correlation hole to −1 electron[11]). Furthermore, the energy improvement obtained with the GU modification appears to be a result of partial cancellation of the positive effect on the energy of this modification and the essentially negative BB error. This cancellation is far from perfect in the bond dissociation region, which is reflected in the large GU errors in this region for a number of prototype molecules (Refs. 12 and 13 and Secs. IV and V). We will discuss this point in further detail when proposing corrections to the BB functional in Sec. III.

A good test of the DMFT methods is the calculation of molecular potential energy curves, which is known to be a challenging task for approximate quantum chemical methods. The latter is true, in particular, for the otherwise successful methods of density functional theory (DFT), for which even the simple H_2 molecule with a dissociating σ bond presents a difficult problem. Spin-restricted variants of standard DFT methods, such as the local density approximation and the generalized gradient approximation tend to produce rather large errors for dissociating closed-shell molecules.[14] As was argued in Ref. 6, an adequate approach should be based on an orbital-dependent functional, which involves both the bonding and antibonding orbitals of a dissociating bond. This is, in fact, the characteristic feature of the generalization of the Fermi hole amplitude of Hartree–Fock theory, employing only occupied orbitals, to the full exchange-correlation hole amplitude of Refs. 2, 5, and 15, which involves the "virtual" (weakly occupied) natural orbitals with weights proportional to the $\sqrt{n_i}$. Nevertheless, application of the ensuing DMFT to the potential curves of some prototype molecules revealed deficiencies.[12,13,16–18] In particular, the BB or CH functional produces a consistent overestimation of the absolute value of the total energy (see also Sec. IV and V). On the other hand, the corrected Hartree–Fock (CHF) method, introduced also by Csanyi and Arias[9] provides little or no improvement over the HF method for prototype molecules around the equilibrium distance.[12,16,19] As analyzed in Ref. 16, this is a consequence of the implicit restriction of the CHF method (and the Bogoliubov method that is equivalent to it[19]) that its Coulomb hole is definite negative, which is certainly far from true for systems where Hartree–Fock is a reasonable zero-order wave function. The GU modification[10] yields mixed results, it often improves

around the equilibrium geometry, but it produces rather large errors for the dissociating H_2 (Ref. 12) and LiH (Ref. 17) molecules.

Further improvement of DMFT is clearly required. In Ref. 20 an approximate functional of the two-electron J and K integrals with $\{\chi_i\}$ has been derived from the theory of the antisymmetrized products of strongly orthogonal geminals and in Ref. 21 the NO occupations n_i in an approximate functional were obtained as diagonal elements of an idempotent matrix, the elements of which represent the variational parameters to be optimized. In Ref. 22 the "phase dilemma" of DMFT is discussed, i.e., the proper choice of the sign of contributions to the xc functional of the terms with cross products of NOs.

In the present paper corrections to the BB functional are proposed (BBCn), which retain the abovementioned important correlating orbital structures of the BB functional, while introducing a number of physically motivated repulsive corrections. In Sec. II the original BB ansatz and the approximations behind it are discussed in both the prototype two-electron case and in the general N-electron case. In Sec. III three variants, BBC1–BBC3, are put forward. The first correction (BBC1) changes the sign in Eq. (1.2) of the cross products $\sqrt{n_a n_b}\chi_a(\mathbf{r}_1)\chi_a(\mathbf{r}_2)\chi_b(\mathbf{r}_1)\chi_b(\mathbf{r}_2)$ between different weakly occupied NOs χ_a and χ_b. A theoretical justification of this correction is that in the two-electron case it brings the approximate expression for ρ_2 closer to the exact one. The second correction (BBC2) reduces (on top of BBC1) the xc interactions in BB between different strongly occupied NOs χ_i and χ_j, $-\sqrt{n_i n_j}\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)/r_{12}$, to the exchange-type interactions $-\frac{1}{2}n_i n_j\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)/r_{12}$. We define here the strongly occupied NOs as the set of $N/2$ NOs with the highest occupation numbers. The third BBC variant (BBC3) applies (on top of BBC1 and BBC2) a correction similar to the BBC2 correction, but now for the interaction of the antibonding NO of the dissociating bond with all strongly occupied NOs, except the corresponding bonding one. The original BB form needs to be retained for the bonding-antibonding pair, since it is precisely the required form to get the left-right correlation right in the case of dissociation.[2,6] BBC3 also applies the GU correction of omitting certain diagonal terms in the Hartree and xc energies for all NOs except the bonding and the antibonding ones. This selective application of the GU correction retains the qualitatively correct BB description of the two-electron bond, which makes an important numerical difference with the full GU correction. In Sec. IV the BBC functionals with $\{\chi_i\}$ and $\{n_i\}$ taken from *ab initio* multireference configuration interaction (MRCI) calculations in large correlation-consistent basis sets are applied to potential curves of a number of prototype few-electron σ-bonded molecules H_2, LiH, Li_2, BH, HF and to the atoms He, Be, and Ne. BBC greatly improves the quality of the DMFT molecular potential energy curves compared to the uncorrected BB and BB-GU ones. The best performance in these post-CI calculations is achieved with the BBC2 variant. In Sec. V the results of self-consistent DMFT calculations are presented. Again, BBC greatly improves the quality of the BB potential curves. The best performance in the self-consistent calculations is achieved with the BBC3 variant. In Sec. VI implications of the present results for DMFT, DFT, and many-electron theory are considered.

II. THE BB FUNCTIONAL

The BB electronic energy functional[2,5] is based on a simple ansatz for the xc hole ρ_{xc}^{hole} (N electron closed-shell systems are considered) which is defined by

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)\rho_{xc}^{hole}(\mathbf{r}_2|\mathbf{r}_1), \tag{2.1}$$

where $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ is the pair density and ρ is the electron density,

$$\rho(\mathbf{r}_1) = \sum_i n_i|\chi_i(\mathbf{r}_1)|^2, \tag{2.2}$$

with n_i being the occupation of the NO χ_i (we work here in the spin-restricted form, suitable for the closed-shell molecules we are dealing with). The ansatz represents ρ_{xc}^{hole} as the square of the amplitude φ_{xc}^{hole},

$$\rho_{xc}^{hole}(\mathbf{r}_2|\mathbf{r}_1) = -|\varphi_{xc}^{hole}(\mathbf{r}_2|\mathbf{r}_1)|^2, \tag{2.3}$$

which is exactly possible in the exchange-only case,[7,23] if we use $\varphi_x^{hole}(\mathbf{r}_2|\mathbf{r}_1) = \Sigma_{i=1}^{N/2}\sqrt{n_i/\rho(\mathbf{r}_1)}\chi_i^*(\mathbf{r}_1)\chi_i(\mathbf{r}_2)$ [all $n_i=2$ ($i \leqslant N/2$)]. When the amplitude $\varphi_{xc}^{hole}(\mathbf{r}_2|\mathbf{r}_1)$ is expanded in the NOs $\chi_i(\mathbf{r}_2)$, with $\mathbf{r}_1$-dependent coefficients $c_i(\mathbf{r}_1)$, symmetry and normalization requirements for $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ lead (apart from a phase factor) to an expression for $c_i(\mathbf{r}_1)$ in terms of χ_i and n_i as follows

$$\varphi_{xc}^{hole}(\mathbf{r}_2|\mathbf{r}_1) = \sum_i \frac{\sqrt{n_i}\chi_i^*(\mathbf{r}_1)}{\sqrt{\rho(\mathbf{r}_1)}}\chi_i(\mathbf{r}_2). \tag{2.4}$$

The choice of complex phase for $\chi_i(\mathbf{r}_1)^*$ is arbitrary, and has been made for smooth connection to the exchange type integrals for (strongly) occupied orbitals. We are dealing with real orbitals and will drop the complex phases. From Eqs. (2.1), (2.3), and (2.4) the expression (1.2) for ρ_2^{BB} follows which, in turn, determines the electron-electron interaction energy functional

$$E_{ee}^{BB} = \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{2}\sum_{i,j}\sqrt{n_i n_j} \times \int \frac{\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2. \tag{2.5}$$

This orbital functional for the correlated total energy has been derived for and has been applied to the many-electron case,[2,5] where it proved to be overbinding. This deficiency was already mentioned in the Introduction. To prepare for the modifications to be proposed in the following section, it is instructive to consider the application of E_{ee}^{BB} in the two-electron case. The ansatz (2.4) for the hole amplitude has in fact been shown to fully incorporate the effects of correlation in two limiting two-electron cases, namely, the nondynamical correlation in the dissociating electron pair bond (stretched H_2) and the dynamical correlation in the case of two-electron ions with $Z>2$ (the He isoelectronic series). The two-electron cases are particularly interesting, since the exact wave function $\Psi(1,2)$ attains the particularly simple

form (1.1) in the natural orbital expansion.[3] The expansion coefficients c_i are determined by the n_i up to a phase factor $f_i = \pm 1$,

$$c_i = f_i\sqrt{n_i/2}. \tag{2.6}$$

From Eqs. (1.1) and (2.6) the exact ρ_2 of the two-electron system reads

$$\begin{aligned}\rho_2(\mathbf{r}_1,\mathbf{r}_2) &= 2\int ds_1 ds_2 \Psi(1,2)\Psi^*(1,2)\\ &= \sum_i n_i|\chi_i(\mathbf{r}_1)|^2|\chi_i(\mathbf{r}_2)|^2 + \Bigg[\sum_{a>1} f_1 f_a\sqrt{n_1 n_a}\chi_1(\mathbf{r}_1)\\ &\times\chi_a^*(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_a^*(\mathbf{r}_2) + \sum_{a>b>1} f_a f_b\sqrt{n_a n_b}\chi_a(\mathbf{r}_1)\\ &\times\chi_b^*(\mathbf{r}_1)\chi_a(\mathbf{r}_2)\chi_b^*(\mathbf{r}_2) + \text{c.c.}\Bigg].\end{aligned} \tag{2.7a}$$

The phase factors f_i show up in the second and third sums of Eq. (2.7a), accompanying the cross products of the weakly occupied NOs χ_a with the strongly occupied NO χ_1 and the cross products between weakly occupied NOs χ_a and χ_b, respectively. Then, using the fact that f_a tends to be negative if the dominant coefficient is chosen to be positive,[24] one arrives at

$$\begin{aligned}\rho_2(\mathbf{r}_1,\mathbf{r}_2) &= \sum_i n_i|\chi_i(\mathbf{r}_1)|^2|\chi_i(\mathbf{r}_2)|^2 + \Bigg[-\sum_{a>1}\sqrt{n_1 n_a}\chi_1(\mathbf{r}_1)\\ &\times\chi_a^*(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_a^*(\mathbf{r}_2) + \sum_{a>b>1}\sqrt{n_a n_b}\chi_a(\mathbf{r}_1)\\ &\times\chi_b^*(\mathbf{r}_1)\chi_a(\mathbf{r}_2)\chi_b^*(\mathbf{r}_2) + \text{c.c.}\Bigg].\end{aligned} \tag{2.7b}$$

Comparing ρ_2^{BB} of Eq. (1.2) with the exact ρ_2 of Eq. (2.7) we note that the BB approximation of writing the xc hole as the square of an amplitude [Eq. (2.3)] which leads to Eq. (1.2) could be considered as amounting to two separate approximations. In the first place the first sum of Eq. (2.7) is approximated as the product $\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$ plus the diagonal terms in the double sum of Eq. (1.2),

$$\begin{aligned}\sum_i n_i|\chi_i(\mathbf{r}_1)|^2|\chi_i(\mathbf{r}_2)|^2 &\approx \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\\ &- \sum_i n_i|\chi_i(\mathbf{r}_1)|^2|\chi_i(\mathbf{r}_2)|^2.\end{aligned} \tag{2.8}$$

This is valid in the two limiting cases of purely dynamical correlation when $n_1 \approx 2$ and $n_{i>1} \approx 0$ (the He isoelectronic series) and of purely nondynamical correlation (dissociated H_2) when $n_1 \approx n_2 \approx 1$ and $n_{i>2} \approx 0$.[2,5] Note, that the approximation (2.8) provides for the normalization condition

$$\int \rho_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = (N-1)\rho(\mathbf{r}_1) \tag{2.9}$$

since the other terms in Eq. (2.7) do not contribute to this integral, and Eq. (2.8) leads immediately to Eq. (2.9). The second approximation is a change of the positive sign of the cross products between weakly occupied NOs in the last sum of Eq. (2.7) to the negative sign of the corresponding terms in Eq. (1.2). This approximation is required in order that the xc hole $\rho_{\mathrm{xc}}^{\mathrm{hole}}$ could be represented as minus the square of the hole amplitude $\varphi_{\mathrm{xc}}^{\mathrm{hole}}$, Eq. (2.3). Though this representation has been used to arrive at Eq. (2.4) and hence at Eq. (1.2), the condition (2.3) is not a necessary attribute of the rigorous theory and, for example, the xc part of the exact pair density (2.7) does not obey it. The erroneous negative sign of these terms in E_{ee}^{BB} may be a source for its being too negative, so it appears natural to adhere to the + sign of the last sum in the exact expression (2.7), which is one of the corrections to be discussed in the following section.

Note that the abovementioned BB approximations preserve the important second term in Eq. (2.7) with (minus) the cross products $-[\sqrt{n_1 n_a}\chi_1(\mathbf{r}_1)\chi_a^*(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_a^*(\mathbf{r}_2) + \text{c.c.}]$, so that it passes unchanged from Eq. (2.7) to Eq. (1.2), apart from a change of the complex phases, which arise from the specific choice of phase for the weakly occupied NOs (the same as for the strongly occupied ones) which was made in Eq. (1.2). This could be changed in Eq. (1.2), but we will, as noted above, refrain from keeping track of the complex phases. For the dissociating H_2 molecule this term reduces (see the Introduction) to $-[\sigma_g(\mathbf{r}_1)\sigma_u(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\sigma_u(\mathbf{r}_2) + \text{c.c.}]$. Taken together with the corresponding diagonal terms with $-|\sigma_g(\mathbf{r}_1)|^2|\sigma_g(\mathbf{r}_2)|^2$ and $-|\sigma_u(\mathbf{r}_1)|^2|\sigma_u(\mathbf{r}_2)|^2$ which arise in the approximation (2.8), this term produces the BB xc hole

$$\begin{aligned}\rho_{\mathrm{xc}}^{\mathrm{hole}}(\mathbf{r}_2|\mathbf{r}_1) \approx -\frac{1}{\rho(\mathbf{r}_1)}\{&|\sigma_g(\mathbf{r}_1)|^2|\sigma_g(\mathbf{r}_2)|^2\\ &+ [\sigma_g(\mathbf{r}_1)\sigma_u(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\sigma_u(\mathbf{r}_2) + \text{c.c.}]\\ &+ |\sigma_u(\mathbf{r}_1)|^2|\sigma_u(\mathbf{r}_2)|^2\},\end{aligned} \tag{2.10}$$

which is correctly localized around the reference electron at $\mathbf{r}_1$, i.e., when $\mathbf{r}_1$ is in the neighborhood of atom H_A, $\rho_{\mathrm{xc}}^{\mathrm{hole}}(\mathbf{r}_2|\mathbf{r}_1 \in \Omega_A) \approx -|a(\mathbf{r}_2)|^2$, and when $\mathbf{r}_1$ is in the neighborhood of H_B, $\rho_{\mathrm{xc}}^{\mathrm{hole}}(\mathbf{r}_2|\mathbf{r}_1 \in \Omega_B) \approx -|b(\mathbf{r}_2)|^2$. Note, that in the general N-electron case the BB ansatz (1.2) contains similar cross products $-\sqrt{n_i n_j}\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)$, $(i\ j)$, for all NOs. Then, the cross products $-[\sqrt{n_i n_a}\chi_i(\mathbf{r}_1)\chi_a(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_a(\mathbf{r}_2) + \text{c.c.}]$ between strongly occupied NOs χ_i, $i \leqslant N/2$, and weakly occupied NOs χ_a, $a > N/2$, represent a natural generalization of the abovementioned two-electron structure $-[\sqrt{n_1 n_a}\chi_1(\mathbf{r}_1)\chi_a(\mathbf{r}_1)\chi_1(\mathbf{r}_2)\chi_a(\mathbf{r}_2) + \text{c.c.}]$.

Terms for which the analysis of the two-electron case, with only one occupied orbital, does not yield a clue, are the cross products $-\sqrt{n_i n_j}\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)$, $(i\ j \leqslant N/2)$, between different strongly occupied NOs. We will identify these terms as another source for the overbinding of E_{ee}^{BB}. The corresponding correction as well as other repulsive corrections will be presented in the following section.

III. REPULSIVE CORRECTIONS: THE BBC*n* FUNCTIONALS

The first repulsive correction to BB (BBC1) proposed in this paper restores the positive phase of the cross products between weakly occupied NOs as it appears in the accurate two-electron ρ_2 of Eq. (2.7). To accomplish this, we introduce the corresponding sign correction (C1) ρ_2^{C1} to ρ_2^{BB} of Eq. (1.2).

$$\rho_2^{\mathrm{BBC1}}(\mathbf{r}_1,\mathbf{r}_2)=\rho_2^{\mathrm{BB}}(\mathbf{r}_1,\mathbf{r}_2)+\rho_2^{\mathrm{C1}}(\mathbf{r}_1,\mathbf{r}_2), \tag{3.1}$$

which only makes this restoration, while preserving the approximation (2.8). Comparing Eq. (1.2) with Eq. (2.7), one finds that ρ_2^{C1} has the general form

$$\rho_2^{\mathrm{C1}}(\mathbf{r}_1,\mathbf{r}_2)=2\sum_{a,b\neq a>N/2}\sqrt{n_a n_b}\chi_a(\mathbf{r}_1)\chi_b(\mathbf{r}_1)\chi_a(\mathbf{r}_2)\chi_b(\mathbf{r}_2), \tag{3.2}$$

which is valid in the two-electron case and can also be applied as a correction to the ansatz (1.2) in the N-electron case. The corresponding electron-electron interaction energy functional E_{ee}^{BBC1} has the form

$$E_{ee}^{\mathrm{BBC1}}=E_{ee}^{\mathrm{BB}}+E_{ee}^{\mathrm{C1}}, \tag{3.3}$$

where

$$E_{ee}^{\mathrm{C1}}=\sum_{a,b\neq a>N/2}\sqrt{n_a n_b}\int\frac{\chi_a(\mathbf{r}_1)\chi_b(\mathbf{r}_1)\chi_a(\mathbf{r}_2)\chi_b(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2. \tag{3.4}$$

The positive correction that we make inhibits the representation of the xc hole corresponding to ρ_2^{BBC1} as minus the square of a hole amplitude, as in Eq. (2.3). However, the correction C1 brings ρ_2^{BBC1} closer to Eq. (2.7) in the two-electron case. Besides, $\rho_2^{\mathrm{BBC1}}(\mathbf{r}_1,\mathbf{r}_2)$ has the correct symmetry with respect to permutation of the electron coordinates $\mathbf{r}_1,\mathbf{r}_2$ and it satisfies the normalization condition (2.9). There is no compelling reason to stick to the initial ansatz that the hole be written as minus the square of an amplitude. We will therefore drop this assumption and will take as our only purpose to provide an accurate approximation to the xc energy.

The second repulsive correction of this paper (C2) is applied on top of BBC1 to the xc interaction between different strongly occupied NOs χ_i and χ_j, $i,j\leqslant N/2$. As was pointed out in the previous sections, this interaction is represented for the i,j pair (and similarly for the j,i pair) with the term $-\frac{1}{2}\sqrt{n_i n_j}\int\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)/r_{12}d\mathbf{r}_1 d\mathbf{r}_2=-\frac{1}{2}\sqrt{n_i n_j}K_{ij}$. This reduces to the normal exchange interaction, which just has the prefactor -1 in front of the K_{ij} integral, when the orbitals are fully occupied, $n_i=n_j=2$. In the correlated case, the occupation numbers start to decrease from 2.0, and the $-\frac{1}{2}\sqrt{n_i n_j}$ factors become less negative than the full (Hartree–Fock) exchange factor -1. If one takes, however, the exchange-type part of the exact pair density, which can be obtained from the exact one-particle density matrix γ as the product $-(1/4)\gamma(\mathbf{r}_1,\mathbf{r}_2)\gamma(\mathbf{r}_2,\mathbf{r}_1)$, one would obtain the off-diagonal terms $-\frac{1}{4}n_i n_j\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)/r_{12}$ in the energy integrand. This of course reduces to pure Hartree–Fock exchange $(-K_{ij})$ in the case $n_i=n_j=2$, but when the occupation numbers start to decrease from 2.0, the factor $-n_i n_j/4$ is less negative even than $-\sqrt{n_i n_j}/2$. We have inferred that the latter terms are indeed too negative, the Coulomb correlation being expressed primarily by the cross terms between strongly and weakly occupied NOs, not between different strongly occupied NOs. We therefore reduce the xc interaction between strongly occupied NOs, replacing for each orbital pair the xc interaction $-\frac{1}{2}\sqrt{n_i n_j}\int\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)/r_{12}d\mathbf{r}_1 d\mathbf{r}_2$ with the exchange-type interaction $-\frac{1}{4}n_i n_j\int\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)/r_{12}d\mathbf{r}_1 d\mathbf{r}_2$. This is effected by the correction ρ_2^{C2} to ρ_2^{BBC1}

$$\rho_2^{\mathrm{BBC2}}(\mathbf{r}_1,\mathbf{r}_2)=\rho_2^{\mathrm{BBC1}}(\mathbf{r}_1,\mathbf{r}_2)+\rho_2^{\mathrm{C2}}(\mathbf{r}_1,\mathbf{r}_2), \tag{3.5}$$

where

$$\rho_2^{\mathrm{C2}}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{i,j\neq i\leqslant N/2}\left(\sqrt{n_i n_j}-\frac{1}{2}n_i n_j\right)\times\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2). \tag{3.6}$$

The corresponding BBC2 energy functional is

$$E_{ee}^{\mathrm{BBC2}}=E_{ee}^{\mathrm{BBC1}}+E_{ee}^{\mathrm{C2}}, \tag{3.7}$$

where

$$E_{ee}^{\mathrm{C2}}=\frac{1}{2}\sum_{i,j\neq i\geqslant N/2}\left(\sqrt{n_i n_j}-\frac{1}{2}n_i n_j\right)\times\int\frac{\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_j(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2. \tag{3.8}$$

Since both corrections C1 and C2 change only the orbital cross products in ρ_2, the function ρ_2^{BBC2} of Eq. (3.5) also satisfies the normalization condition (2.9).

The third BBC variant (BBC3) applies (on top of BBC1 and BBC2) a correction like BBC2 but now for the interaction of the antibonding NO χ_r of the dissociating bond with all strongly occupied NOs, except the corresponding bonding one. In addition, BBC3 applies the GU correction[10] to all NOs, except the bonding and the antibonding ones. This means that in Eq. (2.5) in the Coulomb term $(1/2)\int\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)/r_{12}d\mathbf{r}_1 d\mathbf{r}_2$, the $i=j$ terms describing self-interaction of electrons in the same orbital with the same spin are omitted, amounting to a correction $-\frac{1}{4}n_i^2\chi_i(\mathbf{r}_1)^2\chi_i(\mathbf{r}_2)^2/r_{12}$ to the Coulomb energy integrand. In the xc term the corresponding diagonal terms are omitted, which is a correction $\frac{1}{2}\sqrt{n_i^2}\chi_i(\mathbf{r}_1)^2\chi_i(\mathbf{r}_2)^2/r_{12}$ to the xc energy integrand. In the Hartree–Fock case with $n_i=n_j=2$ the cancellation of these diagonal terms would be automatic, which is the usual correction by the exchange terms of the spurious self-interaction in the Coulomb term. In the present case, the GU approximation, which is only justified pragmatically (it works in the right direction), introduces a positive correction of the form $\left(-\frac{1}{4}n_i^2+\frac{1}{2}n_i\right)J_{ii}$. The factor $-\frac{1}{4}n_i^2+\frac{1}{2}n_i$ goes through zero for $n_i=0$ and $n_i=2$ and has a maximum for $n_i=1$. So this is a relatively small correction when applied to strongly occupied orbitals $(n_i\approx 2)$ and to weakly occupied orbitals $(n_i\approx 0)$. Denoting the bonding/antibonding pair of orbitals as the orbitals with numbers $N/2$ and r, the occupations $n_{N/2}$ and n_r deviate most from 2 and 0, equalizing at 1 at the dissociation limit. Because of this the full GU correction (applied also to $\chi_{N/2}$ and χ_r) would distort the correlation structure (2.10), which is essential for the left-right correlation in the dissociating bond. This distortion (as will be shown in the next sections) produces a dramatic deterioration of some molecular curves in the dissociation region. We therefore will not apply the GU correction for the bonding-

antibonding pair of orbitals with occupation numbers differing strongly from 2 and 0. The resulting ρ_2^{BBC3} can be expressed as follows:

$$\rho_2^{\mathrm{BBC3}}(\mathbf{r}_1,\mathbf{r}_2) = \rho_2^{\mathrm{BBC2}}(\mathbf{r}_1,\mathbf{r}_2) + \rho_2^{\mathrm{C3}}(\mathbf{r}_1,\mathbf{r}_2), \tag{3.9}$$

where

$$\rho_2^{\mathrm{C3}}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{i<N/2} \left(\sqrt{n_i n_r} - \frac{1}{2} n_i n_r \right) \times [\chi_i(\mathbf{r}_1)\chi_r(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_r(\mathbf{r}_2) + \mathrm{c.c.}] + \sum_{i\neq N/2,r} \left(n_i - \frac{1}{2} n_i^2 \right) \chi_i(\mathbf{r}_1)^2 \chi_i(\mathbf{r}_2)^2. \tag{3.10}$$

The corresponding BBC3 energy functional is

$$E_{ee}^{\mathrm{BBC3}} = E_{ee}^{\mathrm{BBC2}} + E_{ee}^{\mathrm{C3}}, \tag{3.11}$$

where

$$E_{ee}^{\mathrm{C3}} = \sum_{i<N/2} \left(\sqrt{n_i n_r} - \frac{1}{2} n_i n_r \right) \times \int \frac{\chi_i(\mathbf{r}_1)\chi_r(\mathbf{r}_1)\chi_i(\mathbf{r}_2)\chi_r(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \sum_{i\neq N/2,r} \left(n_i - \frac{1}{2} n_i^2 \right) \int \frac{\chi_i(\mathbf{r}_1)^2 \chi_i(\mathbf{r}_2)^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \tag{3.12}$$

Equations (3.10) and (3.12) are valid for molecules with a single bond, which are considered in this paper, but their generalization for the case of multiple bonds is straightforward. The selective application of the GU correction in BBC3 as well as other corrections of this paper preserve the important orbital structure (2.10) of the original BB, which is responsible for the proper description of nondynamical electron correlation in the dissociating bond. Unlike other corrections of this section, the GU correction [even if selectively applied in Eqs. (3.10) and (3.12)] does not preserve the normalization condition (2.9). However, as will be shown in Sec. V, the potential energy curves obtained with the self-consistent DMFT calculations with BBC3 provide the best agreement with the benchmark full CI (FCI) and MRCI curves.

IV. POST-CI CALCULATIONS OF POTENTIAL ENERGY CURVES WITH THE BBC FUNCTIONALS

Calculations with the NOs $\{\chi_i\}$ and occupations $\{n_i\}$ obtained from MRCI calculations are of importance for further development of DMFT. Indeed, a successful DMFT functional should reproduce these quantities, so that an assessment of the quality of the proposed functionals with the "best" $\{\chi_i\}$ and $\{n_i\}$ is in order.

Figures 1–5 display the potential energy curves for the prototype σ-bonded molecules H_2, LiH, Li_2, BH, and HF obtained in this post-CI way with the BBC functionals proposed in the preceding section. They are compared with the potential curves obtained with a multireference single and double CI (MRSDCI) with the ATMOL package[25] and they are also compared with the BB and GU curves [the curves labeled GU apply the full GU correction of omitting the same-spin diagonal $i=j$ terms in the Hartree energy and the diagonal terms in the xc energy of the BB expression, Eq. (2.5), in both cases for all orbitals]. The correlation-consistent ba-

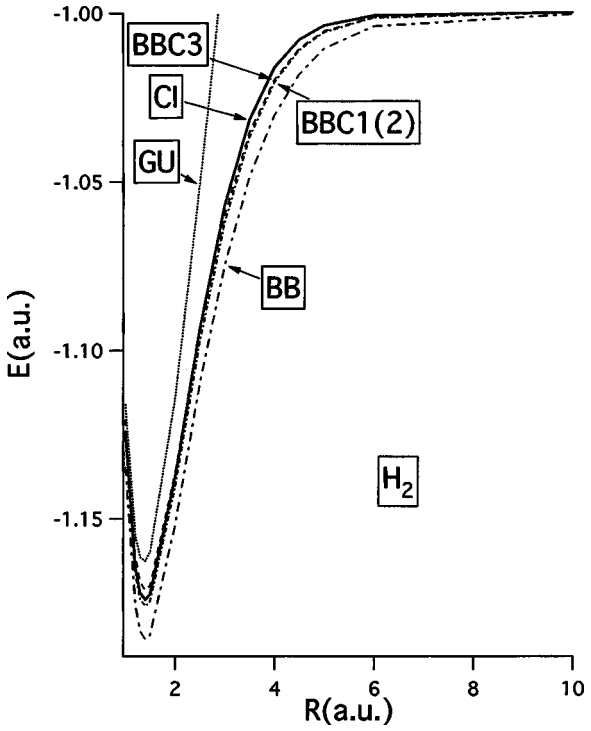

FIG. 1. Energy curves for the H_2 molecule with NOs and NO occupation numbers from full CI calculations in the cc-pV5Z basis. The drawn curve is the full CI curve (labeled CI), the other labels are defined in the text.

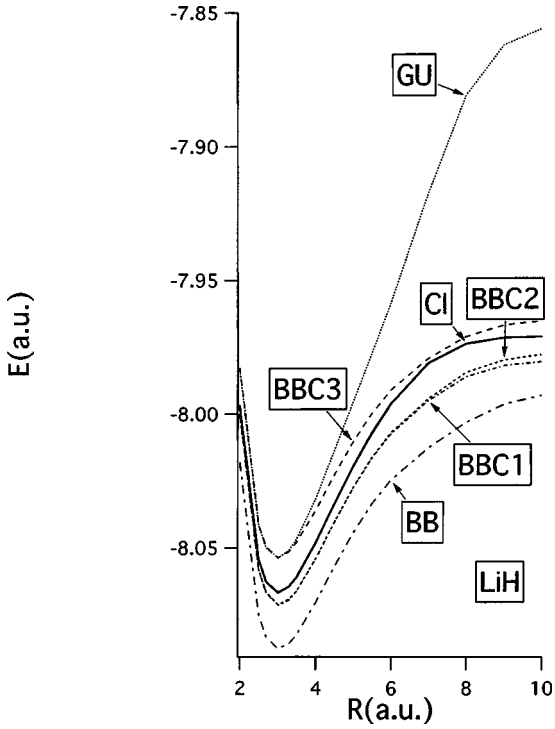

FIG. 2. Energy curves for the LiH molecule with NOs and NO occupation numbers from MRSDCI calculations with the cc-pV5Z basis on H and aug-cc-pCVQZ on Li.

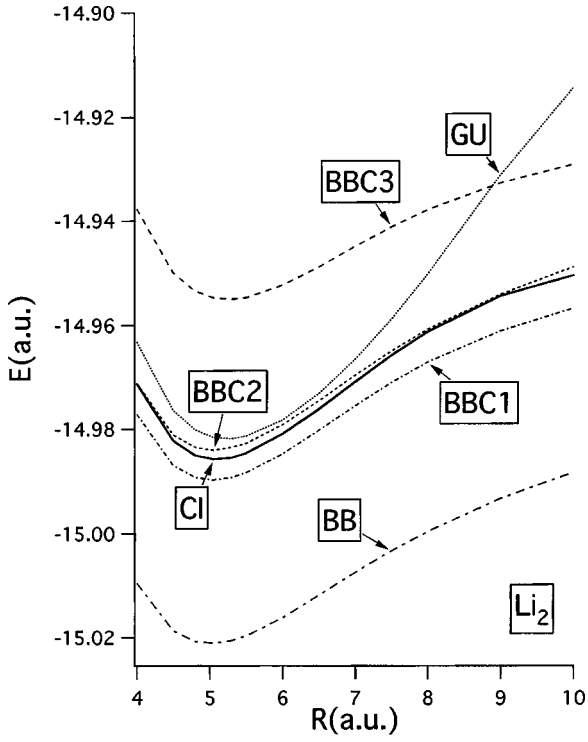

FIG. 3. Energy curves for the Li_2 molecule with NOs and NO occupation numbers from MRSDCI calculations with the aug-cc-pCVQZ on Li.

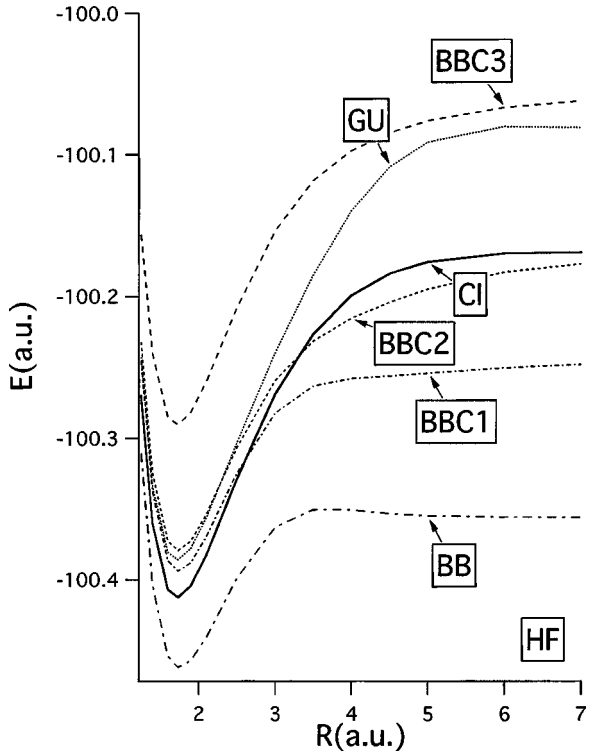

FIG. 5. Energy curves for the HF molecule with NOs and NO occupation numbers from MRSDCI calculations with the cc-pV5Z basis on H and aug-cc-pCVQZ on F.

sis sets are employed in these calculations, which are rather more extended and more adapted to treat electron correlation than the basis sets commonly used in molecular self-consistent DMFT calculations. For H and He atoms the calculations are performed in the correlation-consistent polarized valence 5-zeta basis sets[26,27] (cc-pV5Z) and for heavier atoms the correlation-consistent polarized core-valence quadruple zeta augmented (aug-cc-pCVQZ) basis sets[28,29] are used. NOs $\{\chi_i\}$ and their occupations $\{n_i\}$ obtained with MRSDCI have been used in Eqs. (3.1)–(3.12) to produce the BB, BBC*n*, and GU electronic energies.

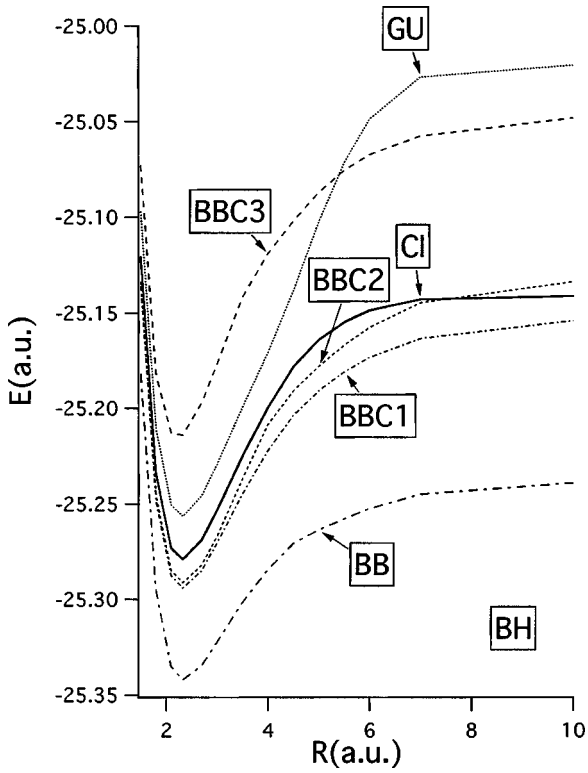

FIG. 4. Energy curves for the BH molecule with NOs and NO occupation numbers from MRSDCI calculations with the cc-pV5Z basis on H and aug-cc-pCVQZ on B.

Since two-electron systems in general, and stretched H_2 in particular, served as the DMFT paradigm, we start our discussion with the potential curves of Fig. 1 for the H_2 molecule. With the scale chosen, it clearly displays, first of all, the well-known failure of the GU approximation. The latter consistently underestimates the H_2 energy and the corresponding error increases dramatically with the bond length $R(\mathrm{H-H})$, so that already at $R=2.5$ a.u. the GU curve is way off the FCI one. The reason for this is the deficiency of the GU correction for NO occupations n_i that deviate appreciably from 2 or 0, which is the case for the singly occupied frontier NOs σ_g and σ_u of the dissociating H_2. In this case the GU modification produces a deficient (not attractive enough) xc hole

$$\rho_{\mathrm{xc}}^{\mathrm{hole(GU)}}(\mathbf{r}_2|\mathbf{r}_1) \approx -\frac{1}{\rho(\mathbf{r}_1)}\left\{\frac{1}{2}|\sigma_g(\mathbf{r}_1)|^2|\sigma_g(\mathbf{r}_2)|^2 + [\sigma_g(\mathbf{r}_1)\sigma_u(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\sigma_u(\mathbf{r}_2) + \mathrm{c.c.}] + \frac{1}{2}|\sigma_u(\mathbf{r}_1)|^2|\sigma_u(\mathbf{r}_2)|^2\right\}, \tag{4.1}$$

which integrates erroneously to $-1/2$ electron. On the other hand, BB consistently overestimates the H_2 energy but, because of the proper form (2.10) of its xc hole, the corre-

TABLE I. Comparison of the total and correlation energies (atomic units) calculated at the molecular equilibrium geometries with BB, GU, BBC*n* (all in the post-CI variant), and MRSDCI.

System	He	Be	Ne	H_2	LiH	Li_2	BH	HF
$-E^{CI}$	2.9032	14.6444	128.8820	1.1739	8.0668	14.9857	25.2791	100.4128
$-E_c^{CI}$	0.0416	0.0714	0.3352	0.0403	0.0795	0.1142	0.1477	0.3442
$-E^{BB}$	2.9119	14.6782	128.9166	1.1857	8.0878	15.0211	25.3422	100.4619
$-E_c^{BB}$	0.0503	0.1052	0.3698	0.0521	0.1005	0.1482	0.2108	0.3679
Error (%)	21	47	10	29	26	31	43	16
$-E^{BBC1}$	2.9047	14.6590	128.8544	1.1759	8.0715	14.9897	25.2941	100.3939
$-E_c^{BBC1}$	0.0431	0.0860	0.3076	0.0423	0.0842	0.1182	0.1627	0.3253
Error (%)	4	20	−8	5	6	4	10	−5
$-E^{BBC2}$	2.9047	14.6571	128.8414	1.1759	8.0712	14.9840	25.2914	100.3795
$-E_c^{BBC2}$	0.0431	0.0841	0.2946	0.0423	0.0839	0.1125	0.1600	0.3109
Error (%)	4	18	−12	5	6	−2	8	−10
$-E^{BBC3}$	2.8975	14.6203	128.8062	1.1712	8.0537	14.9547	25.2141	100.2905
$-E_c^{BBC3}$	0.0361	0.0473	0.2594	0.0376	0.0664	0.0832	0.0827	0.2219
Error (%)	−13	−34	−23	−7	−16	−17	−44	−36
$-E^{GU}$	2.8966	14.6143	128.8531	1.1625	8.0538	14.9816	25.2564	100.3862
$-E_c^{GU}$	0.0352	0.0413	0.3063	0.0289	0.0665	0.1101	0.1250	0.3176
Error (%)	−15	−42	−9	−28	−16	−4	−15	−8

sponding error vanishes at large R(H−H). What is clearly missing in BB at shorter R(H−H) [compared to the exact case, Eq. (2.7)] is the proper positive sign of the cross products of weakly occupied NOs, which is restored with the C1 correction (3.2) of BBC1. In the two-electron case BBC2 coincides with BBC1, while the selective GU correction for weakly occupied NOs makes the BBC3 curve only slightly higher than the FCI and BBC1(2) ones around the equilibrium (see Fig. 1). As a result, all BBC*n* reproduce excellently the FCI curve for H_2 and at large R(H−H) the BBC*n* curves converge somewhat faster than the BB curve to the FCI one.

For other molecules considered GU displays the same trend as for H_2 consistently underestimating molecular total energies (compare Fig. 1 with Figs. 2–5). While this underestimation is not large near equilibrium, it increases sharply with the bond distance, so that the resulting GU curves exhibit incorrect dissociation behavior and are much too deep compared to the MRCI ones. On the other hand, BB consistently overestimates the molecular energies but, unlike the case of H_2, this overestimation appears to increase with the bond distance, which is especially true for the molecules BH and HF with heavier atoms. As a result, in the latter case the BB curves are far too shallow.

A remarkable feature of Figs. 2–5 is that BBC greatly improves the quality of the DMFT potential curves. In particular, the BBC1 and BBC2 curves are much closer to the MRCI curves than the BB or GU ones. The main correction to BB appears to be the phase correction C1 of Eqs. (3.2) and (3.4), though the C2 correction plays an increasingly important role with increasing number of strongly occupied orbitals, the interaction of which determines the size of C2 through Eqs. (3.6) and (3.8). For LiH with only two strongly occupied NOs the BBC1 and BBC2 curves nearly coincide with each other with only a marginal difference at large R(Li−H) (see Fig. 2). Already for Li_2 with three strongly occupied NOs the C2 correction makes a rather important difference (see Fig. 3). While C1 is a dominant correction to BB at all distances R(Li−Li), C2 significantly reduces further the DMFT error, so that the BBC2 curve excellently reproduces that of MRCI. For BH the BBC1 and BBC2 curves nearly coincide with each other around the equilibrium (see Fig. 4), however, the C2 correction increases with the bond length R(B−H), which makes the BBC2 curve definitely closer to the MRCI one in the dissociation region. For HF, though slightly worsening the BBC performance near the equilibrium (see Fig. 5), C2 plays an important role at larger R(F−H) considerably reducing the relatively large discrepancy between the MRCI and BBC1 curves at large R. For the latter two molecules, the combined effect of C1 +C2, incorporated in the BBC2 curve, greatly reduces the large BB error in the dissociation region.

Note that, except for the case of H_2 discussed above (see Fig. 1) and for the dissociating LiH (see Fig. 2), the third BBC correction C3 produces a too high upward shift of the BBC3 curve for Li_2, BH, and HF (see Figs. 3–5). However, this upward shift notwithstanding, the form of the BBC3 curves appears to be surprisingly good, reproducing fairly well the form of the MRCI curves (see Figs. 1–5).

Table I presents the total (E) and correlation (E_c) energies calculated for the abovementioned molecules at the equilibrium distances as well as those calculated for the atoms He, Be, and Ne in the same post-CI manner. Because of the absence of bonds for free atoms, we calculate the BBC3 functional in this case without the corrections to an antibonding orbital. Thus, the C3 correction in Eqs. (3.10) and (3.12) reduces in this case to the GU correction applied to all orbitals, except the last strongly occupied orbital $\chi_{N/2}$. In agreement with the discussion given above, BB consistently overestimates E_c values compared with those obtained with the benchmark CI calculations. In turn, GU and BBC3 consistently underestimate E_c. BBC1 and BBC2 produce similar energies (by definition, for two-electron systems, such as He and H_2, these are the same energies) and they display E_c errors of either sign (see Table I). With this, BBC1 and

BBC2 achieve the best performance among the functionals considered, with the same relatively small average absolute error of E_c of 8% for both functionals.

To sum up, the BBC corrections greatly improve the quality of the BB potential energy curves obtained with non-self consistent DMFT calculations with MRCI $\{\chi_i\}$ and $\{n_i\}$. In this type of calculation the BBC2 functional shows the best overall performance. In the following section it will be shown that the energy lowering due to the self-consistent optimization significantly improves the atomic and molecular energies obtained with the BBC3 functional, so that the latter emerges as the best self-consistent functional.

V. SELF-CONSISTENT CALCULATIONS OF THE POTENTIAL ENERGY CURVES WITH THE BBC FUNCTIONALS

Though the post-CI calculations presented in the preceding section are useful for the assessment and further development of the DMFT methods, in a full-fledged DMFT method all quantities should be calculated in a self-consistent manner. Obviously, a variational, self-consistent energy minimum of an approximate DMFT functional is lower than its energy calculated with any nonvariational NOs and their occupancies, even with the best MRCI $\{\chi_i\}$ and $\{n_i\}$. In particular, while the BBC2 energies obtained in the post-CI calculations are rather close to the MRCI ones (see the preceding section), the self-consistent BBC2 energies appear to be consistently lower than the corresponding MRCI [or full-configuration interaction (FCI) where it was possible to calculate them] values. Since BBC2 is obtained from BBC1 with the repulsive correction C2, the self-consistent BBC1 energies are lower than the already too low BBC2 energies. On the other hand, the C3 repulsive correction, which makes the post-CI BBC3 energies too high, produces self-consistent BBC3 energies that appear to be rather close (and in some cases very close) to the MRCI ones. This discrepancy means, of course, that the self-consistent DMFT NOs and their occupations differ from the corresponding MRCI (close to exact) $\{\chi_i\}$ and $\{n_i\}$. The ultimate goal, of course, is to formulate NO dependent xc functionals that yield self-consistently optimized orbitals that are close to the exact NOs, so the discrepancy between energies based on exact NOs and on optimized orbitals would disappear. We note that there is no proof for variational stability of the functionals we are investigating. For the BB (CH) functional the possibility of variational collapse has been investigated for the H_2 molecule, as a function of basis set and of the number of "active" orbitals ("virtual" orbitals that are allowed to acquire occupations).[16] It was concluded that variational collapse does not show up. This has been confirmed by Herbert and Harriman with larger basis sets and for other systems.[17]

Figures 6–10 display the potential energy curves for the prototype molecules obtained with self-consistent calculations with the BB, GU, and BBC3 functionals. They are compared with the FCI results in the case of H_2, LiH, Li_2, and BH (and He, Be in Table II) or MRSDCI results in the case of HF and Ne. As a natural reference, the restricted Hartree–Fock (HF) curves in the same bases are also included. Because of the computationally more demanding or-

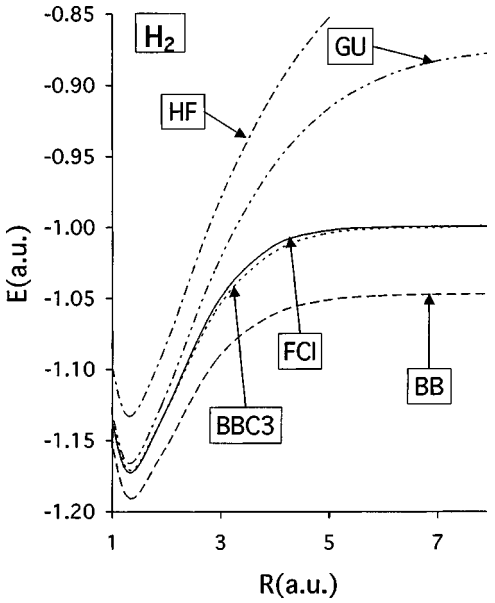

FIG. 6. Energy curves for the molecule H_2 with self-consistent determination of the NOs and NO occupation numbers for each NO functional. For basis see text.

bital optimization, the basis sets are smaller than in the preceding section. The absolute energies of Figs. 6–10 are therefore not directly comparable to those of Figs. 1–5. For atoms the cc-pVQZ (Ref. 26) basis set was employed with the exclusion of the g and one of the f orbitals for Be and Ne. For molecules composed of at least one light atom, i.e., for H_2, LiH, BH, and HF, the correlation-consistent polarized valence triple-zeta basis set (cc-pVTZ) was used from which the f orbital for heavy atoms was excluded, whereas for the Li_2 molecule a smaller cc-pVDZ basis set was used. It should be emphasized that the employed basis sets are still relatively large compared to previous calculations[16,21] and we did not freeze any orbitals throughout the optimization calculations. Fully variational DMFT calculations involve

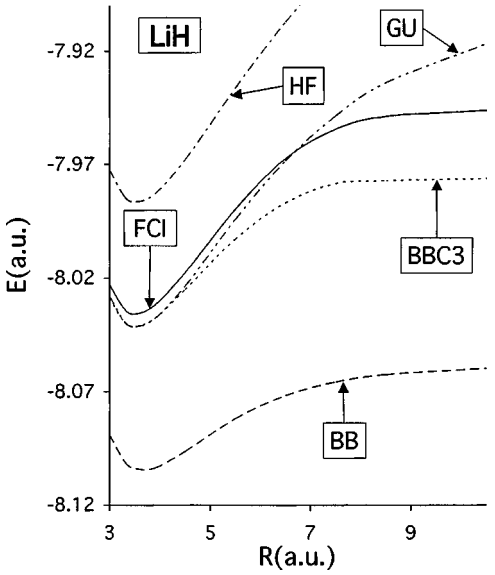

FIG. 7. Energy curves for the LiH molecule with self-consistent determination of the NOs and NO occupation numbers for each NO functional. For basis see text.

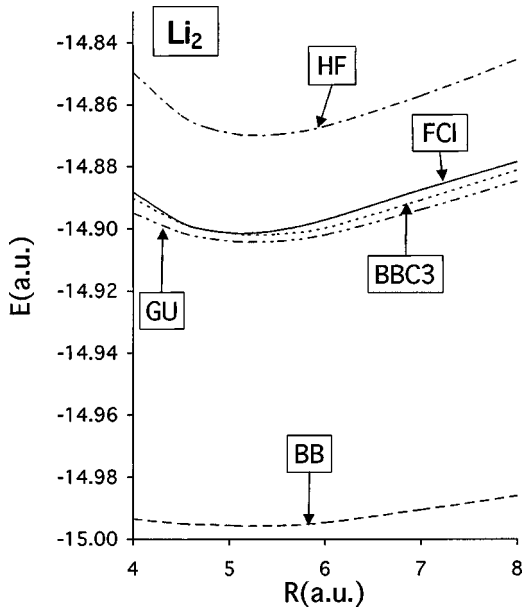

FIG. 8. Energy curves for the Li_2 molecule with self-consistent determination of the NOs and NO occupation numbers for each NO functional. For basis see text.

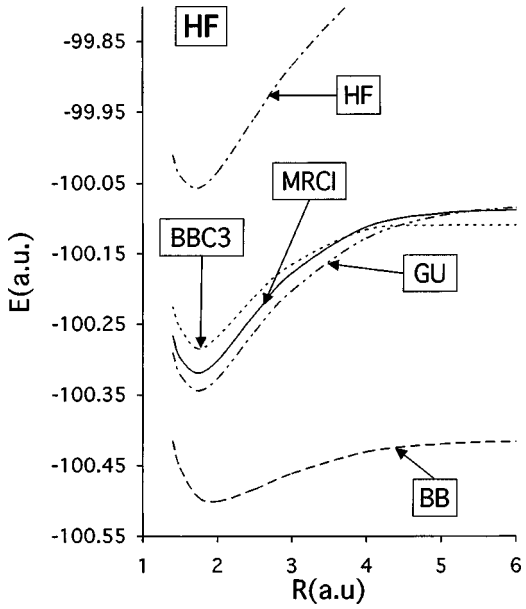

FIG. 10. Energy curves for the HF molecule with self-consistent determination of the NOs and NO occupation numbers for each NO functional. For basis see text.

minimizing the total energy with respect to both natural orbitals and natural occupation numbers. For singlet and triplet ground states of two-electron systems, such a method was developed and applied some time ago by Kutzelnigg.[24] To assure convergence to the minimum and to make the calculations more efficient, we have implemented a two-step procedure. It consists of minimization of the energy with respect to the natural orbitals for fixed occupation numbers and a subsequent variation of the occupancies for the new set of natural orbitals (obtained in the first step). This procedure is repeated until convergence is achieved. The natural orbitals were parametrized according to the orthonormality-preserving scheme presented in Ref. 30 and the quasi-Newton Boyden-Fletcher-Goldfarb-Shannon (BFGS Ref. 31) optimization method was implemented in the first step of the variational procedure described above. To assure that the natural occupancies stay between zero and two and that they sum up to the number of electrons N, we imposed that $n_i = 2\cos^2(p_i)$ and $\Sigma_i n_i = N$. For the optimization of the free parameters $\{p_i\}$ we employed the conjugate gradient Polak–Ribière algorithm.[31]

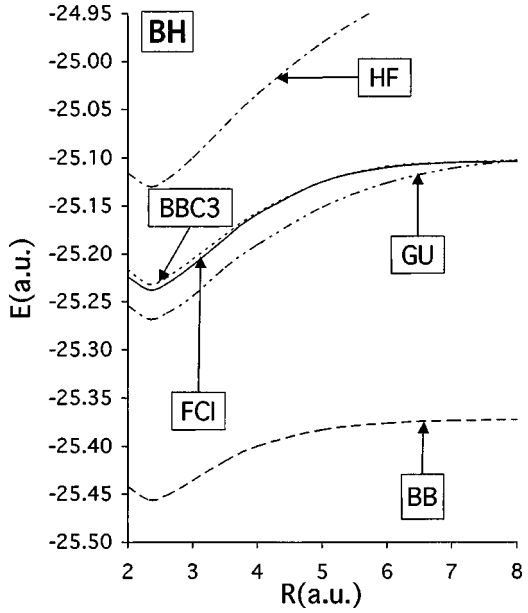

FIG. 9. Energy curves for the BH molecule with self-consistent determination of the NOs and NO occupation numbers for each NO functional. For basis see text.

We start our discussion with the potential curves for the H_2 molecule in Fig. 6. Optimization improves GU close to the equilibrium geometry, but again, due to its deficient xc hole (4.1), it produces a large positive error at large bond lengths. On the other hand, unlike in the post-CI calculations and in agreement with the previous self-consistent calculations,[12,16] BB consistently overestimates the H_2 energy not only near equilibrium, but at all $R(\mathrm{H-H})$ distances (compare Figs. 1 and 6). The apparent reason for this overestimation is the difference between the FCI $\{\chi_i\},\{n_i\}$ and the corresponding quantities produced self-consistently with the over-attractive BB functional. But then, the repulsive corrections of BBC3 remove this error. As a result, BBC3 excellently reproduces the FCI potential curve of H_2 at all $R(\mathrm{H-H})$ (see Fig. 6), the largest BBC3 error is only 3 kcal/mol at $R(\mathrm{H-H})=4$ a.u.

Similar trends in the self-consistent performance of the DMFT functionals follow also for other molecules. Just as in the post-CI calculations of the preceding section, the self-consistent BB greatly overestimates the molecular energies, especially in the dissociation region, so the BB potential curves are much too shallow (see Figs. 7–10). The self-consistent GU curves are also too deep around R_e (except in the case of H_2), but much less so than the BB energies. The self-consistent GU curves dissociate improperly for H_2 and LiH, rising too high as in the post-CI case, though the corresponding error is relatively not as large as that case. In the

TABLE II. Comparison of the total and correlation energies (atomic units) calculated at the molecular equilibrium geometries with the self-consistent BB, GU, BBC3, and MRSDCI (for Ne and HF) or FCI (for other systems) methods.

System	He	Be	Ne	H_2	LiH	Li_2	BH	HF
$-E^{CI}$	2.9024	14.6400	128.8278	1.1723	8.0357	14.9014	25.2376	100.3192
$-E_c^{CI}$	0.0409	0.0671	0.2843	0.0394	0.0492	0.0319	0.1077	0.2616
$-E^{BB}$	2.9141	14.7632	128.9548	1.1904	8.1040	14.9956	25.4560	100.4941
$-E_c^{BB}$	0.0526	0.1903	0.4113	0.0574	0.1175	0.1261	0.3262	0.4365
Error (%)	29	184	45	46	139	295	203	67
$-E^{BBC3}$	2.8976	14.6423	128.8333	1.1705	8.0414	14.9016	25.2320	100.2844
$-E_c^{BBC3}$	0.0361	0.0693	0.2898	0.0375	0.0550	0.0320	0.1022	0.2268
Error (%)	−12	3	2	−5	12	0	−5	−13
$-E^{GU}$	2.8978	14.6578	128.8583	1.1658	8.0414	14.9040	25.2680	100.3441
$-E_c^{GU}$	0.0363	0.0848	0.3148	0.0329	0.0549	0.0345	0.1382	0.2865
Error (%)	−11	26	11	−17	12	8	28	10

other molecules (Li_2, BH and HF) the self-consistent GU curves do not exhibit the large error of the post-CI calculations. The apparent reason for this better performance of the GU approximation is partial cancellation of the positive error, corresponding to the deficient GU xc hole (4.1) and the large negative error of the BB part of the self-consistent functional. For H_2 this cancellation fails (see Fig. 6), for LiH it also does not work well (Fig. 7), while it produces good quality curves for Li_2 (Fig. 8) and HF (Fig. 10), and somewhat less so for BH due to a relatively large error at R_e.

The best overall performance is achieved with the self-consistent BBC3 functional. When one takes into account that the present orbital-dependent exchange-correlation functionals are not essentially more complicated than the HF exchange functional—the most important complication being the additional variability of occupation numbers—the improvement compared to the Hartree–Fock curves in Figs. 6–10 is striking. In particular, BBC3 excellently reproduces the potential energy curves not only for H_2 but also for Li_2 and BH. In fact, the GU curve for Li_2 is already of high quality. However, BBC3 manages to further enhance the DMFT quality at all R(Li–Li) and near R_e the BBC3 curve practically coincides with the FCI one (see Fig. 8). BBC3 also exhibits a remarkably good performance for BH (see Fig. 9). The largest deviation between the FCI and BBC3 curves in this case is only 4 kcal/mol and for larger R(B–H), starting from ca. 4 a.u., both curves coincide with each other. For LiH and HF the performance of BBC3 is somewhat worse. In the former case, the BBC3 curve coincides with the GU one around the equilibrium and both curves are close to but a bit lower than the FCI one in this region (see Fig. 7). However, at larger R(Li–H) the BBC3 and GU curves diverge from each other and from the FCI curve. While the GU curve goes too high, the BBC3 curve goes too low. For the HF molecule the BBC3 curve is too shallow in total, being too high around R_e, and somewhat too low at $R\to\infty$ (see Fig. 10). However, both BBC3 and GU greatly improve upon BB. However, while the GU improvement emerges from the abovementioned cancellation of errors, that of BBC3 comes as a result of successive corrections of Sec. III, which do not distort the correct BB orbital structure (2.10) for the dissociating bond.

Table II presents the self-consistent DMFT and FCI/MRSDCI total and correlation energies calculated for the prototype molecules at the equilibrium bond lengths as well as for the atoms He, Be, and Ne. Comparison with Table I with the post-CI energies shows that, due to the variational effect discussed in the beginning of this section, the self-consistent energies of the DMFT functionals are substantially shifted downwards compared to the corresponding post-CI energies. This downward shift dramatically increases, in general, the overestimation of the correlation energies with BB (see Table II). In turn, the GU and BBC3 self-consistent correlation energies display errors of either sign. In particular, the average absolute error of the GU correlation energies is 14%. The BBC3 functional shows the best performance also at the equilibrium geometry. The BBC3 E_c values are closer to the FCI/MRSDCI ones than the GU values in all cases, except He (for which the BBC3 and GU E_c are nearly the same) and HF (see Table II). The relative error of BBC3 does not increase with the size of a system. Indeed, the largest error of −13% for the ten-electron HF molecule is close to that of −12% for the two-electron He atom. On the other hand, the error for another ten-electron system, the Ne atom is only 2%, while for the six-electron Li_2 the BBC3 E_c coincides with the FCI one. With this, the absolute average E_c error of the self-consistent BBC3 is only 6.5%.

To sum up, the results of the self-consistent DMFT calculations presented in this section show the best overall performance of the BBC3 functional, which greatly improves the quality of the original BB for the potential energy curves as well as the quality of the total and correlation energies for atoms and for molecules at the equilibrium geometry.

VI. CONCLUSIONS

The improved density matrix functionals BBC*n* proposed in this paper employ simple nonempirical corrections to the BB functional. These corrections provide a physically reasonable description of electron exchange and correlation in terms of the NO product structures in the approximate pair-density ρ_2. In particular, the repulsive xc interaction between electrons in weakly occupied NOs, provided with the C1 correction BBC1, corrects the sign of the terms involving products of weakly occupied NOs only to the sign those terms have in the exact ρ_2 for the limiting two-electron case.

On the other hand, the C2 correction reduces the xc interaction of the BB functional between electrons in strongly occupied NOs to the exchange-type interaction that can be written as $-\gamma(\mathbf{r}_1,\mathbf{r}_2)\gamma(\mathbf{r}_2,\mathbf{r}_1)/4$ also for nonidempotent one-matrices (with occupation numbers differing from 2 and 0). In turn, the C3 correction includes the antibonding orbital of a dissociating molecular bond, which formally belongs to the weakly occupied set of orbitals, in the set of orbitals for which this type of interaction (one-matrix exchange) is assumed. In addition, the C3 correction applies a selective cancellation (not for the bonding/antibonding pair of orbitals) of the diagonal terms in the Coulomb and xc interactions, as originally applied by GU for all orbitals.

A remarkable result of the paper is that these simple orbital product structures, based on a qualitatively reasonable description of the xc effects, yield within DMFT rather accurate molecular potential energy curves as well as reasonable correlation energies for prototype atoms and molecules. BBC greatly improves the quality of the BB potential curves in all regions and for all molecules considered and, unlike GU, it does not fail in certain cases such as the dissociating H_2 molecule. This overall good performance of BBC is due to the fact that all the C*n* corrections do not distort the important orbital product terms of the BB functional that describe correlation in the dissociating bond.

BBC reproduces well the correlation energies obtained with FCI/MRSDCI for the equilibrium geometry. The average absolute error of the self-consistent E_c calculated with BBC3 is only 6.5%. The apparent reason for this are the specific orbital product terms involving strongly and weakly occupied NOs, which are introduced with the original BB ansatz and describe both nondynamical and dynamical correlators, and are retained in BBC*n*. However, the virtue of this orbital structure is revealed only when other orbital product terms are corrected, as is done in the case of the BBC*n* functionals. The present results show that for a number of typical systems an accurate approximation to the CI result can be obtained with NO functional. Effectively, a highly correlated result is obtained with an energy expression, which only employs two-index two-electron integrals (the so-called *J* and *K* integrals). In contrast to the Hartree–Fock method, however, these integrals have to be evaluated not only for the limited set of $N/2$ occupied canonical orbitals, but for both strongly and weakly occupied NOs. It is, nevertheless, very gratifying that with such a relatively small extension of the exchange functional of Hartree–Fock theory such a considerable improvement is possible. Although the Hartree–Fock model covers a very large part of the total energy of atoms, and hence of molecules, it should not be forgotten how poor this model is for chemical bonding, i.e., for chemistry (cf. the HF curves in the figures). With errors of typically 25%–100% of the bond energy, it is indeed even a poor zero-order description of bonding. This is reflected in very large errors in individual energy terms such as kinetic energy, electron-nuclear attraction energy (Hartree–Fock densities tend to be very poor), and electron-electron Coulomb repulsion energy. These errors are typically of the same order or even much larger than the bond energy itself.[32–34] It is highly desirable that a (much) better zero-order method for chemical bonding, of essentially self-consistent field level of complexity, be developed. The developments in this paper go some way in this direction.

We shall extend these investigations in both a DMFT and a DFT framework. First, the present BBC will be applied within DMFT to a larger and more varied set of molecules and their reactions. Already, our results for the HF molecule suggest further refinement of BBC. Then, the established discrepancy between the post-CI and self-consistent DMFT calculations is to be addressed. Eventually, a successful DMFT method should reproduce closely both the energies and NOs (and their occupations) of *ab initio* FCI/MRSDCI calculations. If an efficient evaluation of the approximate NOs can be achieved in a Hartree–Fock-like self-consistent field procedure, the NO functionals offer the perspective of a large improvement over the Hartree–Fock model with moderate cost. This would not only yield good energetics on the basis of the NO functionals, but also provide an excellent (natural) orbital basis for a subsequent CI calculation.

The present BBC functional will be applied also within density functional theory (DFT) for which the proper description of the full potential curves is known to be a notoriously difficult problem. In this case, as was proposed in Refs. 6 and 14, instead of NOs and their occupations $\{n_i\}$, the occupied and virtual Kohn–Sham orbitals $\{\phi_i\}$ are to be inserted in the xc functionals with corresponding participation weights $\{w_i\}$. The latter quantities cannot be calculated with the same self-consistent procedure as n_i, rather the w_i are to be obtained as functionals of other KS quantities, for example, as functionals of the KS orbital energies $\{\varepsilon_i\}$ as in Ref. 14. It is currently believed that the next step in refinement of xc functionals in DFT has to involve the introduction of orbital-dependent functionals. While the exact-exchange functional is a natural first choice, it suffers from similar disadvantages as the Hartree–Fock model does.[34] Orbital-dependent functionals should incorporate the effects of correlation from the start in order to be competitive at all with the available density and density-gradient based functionals. The functionals of the type investigated here are such exchange plus correlation including orbital-dependent functionals. The results of this paper prove their viability.

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